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(54) Resilient Compositions

(57) The invention relates to novel resilient compositions useful as surfacing materials and to a method of making the compositions. The resilient composition comprises a cured matrix of a polymer which contains particles of an elastomeric material wherein the polymer is the reaction product of an

active-hydrogen group-containing hydrocarbon polymer, an organic polyisocyanate and moisture. The compositions usually have interconnected voids which renders them free-draining and a further advantage is that they are not normally adversely affected by excess water, e.g. rainfall, during the initial curing period.

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SPECIFICATION

Resilient Compositions

This invention relates to novel resilient compositions and to a method of producing them.

According to one aspect of the present invention, a resilient composition comprises a cured matrix of a polymer which contains particles of an elastomeric material wherein the polymer is the reaction product of an active-hydrogen group-containing hydrocarbon polymer, an organic polyisocyanate and moisture. 5

According to a further aspect of the present invention, a method of producing a resilient composition comprises dispersing a particulate elastomeric material in a polymer matrix which is a reaction mixture comprising an active-hydrogen group-containing hydrocarbon polymer and an organic polyisocyanate, and curing the matrix in the presence of moisture. 10

"Curing" as used in this specification means the interaction between the hydrocarbon polymer, polyisocyanate and moisture and "cured" is to be construed accordingly.

The resilient compositions of the present invention usually have interconnected voids which thus renders them free-draining. They are useful as surfacing materials e.g. as sports surfaces and flooring. 15
The compositions may suitably be formed in situ e.g. by casting the elastomeric material in a matrix of the reaction mixture where required. The moisture may be in the air and/or as added water e.g. steam. During curing, the polymer matrix may also serve to bond the composition to an adjacent substrate. The resilient compositions, during formation, are usually unaffected by excess water and therefore it is not normally necessary to keep a freshly laid surface covered so as to protect it from excess water, e.g. rainfall, during the initial curing period. 20

Preferably the relative proportion by weight of elastomeric material and polymer matrix is in the range from 1:1 to 9:1, more preferably about 5:1.

The resilient compositions are usually water permeable i.e. free draining so that puddles will not form on the surface during moderate to heavy rainfall. (The substrate should also be free-draining). 25
Preferably the resilient compositions can cope with at least 0.5 mm/hour of rainfall and more preferably at least 10 mm/hour. A fairly simple test which can be performed to determine the drainage rate of a resilient composition is as follows: A sample of a resilient composition according to the present invention is placed on an open-topped tin about 60 mm in diameter and a vertical open-ended glass cylinder 50 mm in diameter is pressed firmly in contact with the top surface of the resilient composition to form a watertight seal. (A sealant or gasket may be used to prevent leakages). 40 cc of water is poured into the cylinder to give a depth of approximately 20 mm. The time for the level of water to fall to 10 mm or, if this is more than 1 hour, the distance the level falls in one hour is noted and the drainage rate expressed as mm/hour. 30

Examples of active-hydrogen group-containing hydrocarbon polymers are hydroxy-tipped polybutadiene, polyisoprene, polyisobutylene and a copolymer of butadiene with styrene or acrylonitrile. Hydrogenated hydrocarbon polymers may be used. Preferably the molecular weight of the hydrocarbon polymer is in the range of 400 to 10,000, more preferably 1000 to 3000. The hydrocarbon polymer preferably has active hydrogen groups at least at or adjacent the ends of the molecules. 35 40

The elastomeric material is usually in the vulcanised state in the matrix and may be cellular (closed or open-celled) although it is preferably non-cellular.

Preferably the elastomeric material is prevulcanised i.e. already in the vulcanised state prior to incorporation into the polymer matrix.

Examples of suitable elastomers include natural rubber, styrene/butadiene rubber (SBR) and blends thereof. If desired, particles of whole-tyre scrap (e.g. from United reclaim) may be used i.e. the vulcanised tyre rubber minus lint and bead wires. The waste may have been e.g. ground or shredded. 45

The particle size of the elastomeric material is preferably within the range having a maximum dimension of from 3 cm to particles which will not pass a 200 μ sieve, some preferably within the range from 1.5 cm to 1 mm. 50

Examples of suitable organic polyisocyanates include methylene-bis-aniline-diisocyanate, 4,4'-diphenylmethane diisocyanate which may be carbodiimide modified, other diphenyldiisocyanates, bis(isocyanatophenyl)methane, 1,5-naphthalenediisocyanate, polyphenyl polymethyleneisocyanate, toluene diisocyanates, hexamethylene diisocyanate, dodecamethylene diisocyanate and 1,4-diisocyanatocyclohexane. 55

Examples of active hydrogen groups include hydroxyl, mercaptan, carboxyl and amine. The ratio of the number of functional NCO groups in the polyisocyanate to the number of active hydrogen groups in the active-hydrogen group-containing hydrocarbon-polymer is preferably in the range from 10:1 to 1:1 and more preferably from 4:1 to 3:1. 60

The reaction mixture may be a combination of ingredients or a prepolymer of the hydrocarbon polymer and polyisocyanate. Preferably the hydrocarbon polymer and polyisocyanate are liquid when combined even if it is necessary to heat one or both of them to attain this.

The polymer matrix formed from the reaction mixture may be of a polyurethane, a polyurea or a polyamide and should be resilient.

The resilient compositions of the present invention may also include one or more additives e.g. a catalyst to promote reaction between the hydrocarbon polymer, polyisocyanate and moisture (e.g. a tin compound such as stannous octoate or dibutyl tin dilaurate), filler (e.g. cork, or carbon black), pigment, extender or antioxidant. The limit on the relative amount of additive which may be present may be determined by the degree of permeability of the resilient composition to be produced.

The invention will now be illustrated by the following Examples in which all parts are by weight. Example 1 is included for comparison and does not illustrate the invention.

Example I

A polyurethane prepolymer was made by mixing, and allowing to react at room temperature, 100 parts of a 2000-m.w.t. poly(propylene glycol)diol (Voranol P-2000 ex. Dow) and 62 parts of a liquid modified diphenylmethane diisocyanate (Desmodur PF ex. Bayer). Then 25 parts of this prepolymer and 3 parts of a proprietary 26% dispersion of carbon black in nonylphenol (PUR Black ex. Hoechst) were mixed with 100 parts of whole tyre scrap (ex. United Reclaim) consisting of vulcanised rubber granules having irregular shapes and assorted sizes (none exceeding 0.5 cc). The resulting mixture was trowelled into a metal frame on an out-of-doors tarmacadam site. Heavy rain ensued within minutes of laying and the laid composition soon became water-logged and remained so for some 48 hours because the frame prevented drainage. When the composition was examined some three months later it was found to be of poor quality in that it lacked cohesion and rubber granules could easily be detached from its surface.

Example II

A polyurethane prepolymer was made by mixing and allowing to react at room temperature, 100 parts of a hydroxy-tipped 2800 molecular weight liquid polybutadiene (Poly-BD Resin R-45 HT ex. Arco) and 36 parts of a liquid modified 4,4'-diphenylmethane diisocyanate (Desmodur PF ex. Bayer). Then 25 parts of this prepolymer, 3 parts of the carbon black dispersion used in Example 1 and 0.1 part of dibutyl-tin dilaurate catalyst were mixed with 100 parts of the rubber granules described in Example 1. The mixture was trowelled into a shallow tray which was then totally immersed in water which was left to stand at the ambient temperature (18 to 20°C). After 24 hours the mixture had reacted to form a tough, resilient composition.

The drainage rate for the composition was determined by the earlier described method and the result is given in the Table below. Two further compositions (IIb and IIc) were prepared in the same way as IIa except that in IIb a proportion of the rubber granules was ground to 10 mesh size and in IIc all the rubber granules were ground to 10 mesh size. The drainage rates of these two compositions were determined by the earlier described method and the results are also given in the Table below:

Table

	IIa	IIb	IIc
Rubber granules 10 mesh crumb (passing 1.7 mm aperture but not 1.4 mm aperture)	357	259	0
Dimensions (mm of composition)	99×87×28	102×9×23	104×96×14
Rate of flow (mm/hour)	70,000	7,000	1

(All parts are per 100 parts of polymer matrix).

Example III

In this example the same materials and relative proportions were used as in Example II. The only difference was that the mixture was cast into a shallow tray which was then immediately totally immersed in water. After 48 hours the tray and its contents were removed from the water and left to stand on a level top for 2 months. When examined after this period the composition was found to be of excellent quality and was unaffected by 1000 hours of continuous exposure to an ultraviolet weathering apparatus with intermittent water spray.

Example IV

18 parts of the OH-tipped polybutadiene used in Example II, 7 parts of a form of methylene-bis-aniline diisocyanate containing higher-functionality isocyanates (Suprasec DND), 3 parts of the carbon black dispersion described in Example I and 0.1 part of dibutyl tin dilaurate were mixed with 100 parts of the granulated rubber described in Example I. The mixture was trowelled into a shallow tray which was then totally immersed in water. After 48 hours the tray was removed from the water and left to stand on a bench top. When examined periodically the composition was found to have the quality and ageing resistance of that produced from the same polybutadiene by the method of Example III.

Example V

22 parts of an OH-tipped liquid copolymer of butadiene and 14% by weight acrylonitrile (HTBN from Goodrich) were mixed with 8 parts of Suprasec DND, 3 parts of a carbon black dispersion, 0.1 part of a dibutyl tin dilaurate and 100 parts of granulated rubber. The mixture was trowelled into a shallow tray and left to stand at ambient temperature. After 24 hours the mixture had reacted to form a tough, resilient composition.

Example VI

Example V was repeated using 20 parts of a carboxyl-tipped liquid polybutadiene (CTB from Goodrich) instead of the HTBN. A tough, resilient composition resulted.

10 Claims

1. A resilient composition comprising a cured polymer matrix which contains particles of an elastomeric material wherein the polymer is the reaction product of an active-hydrogen group-containing hydrocarbon polymer, an organic polyisocyanate and moisture. 10
2. A resilient composition according to claim 1, wherein the hydrocarbon polymer comprises polybutadiene. 15
3. A resilient composition according to claim 1, wherein the hydrocarbon polymer comprises polyisoprene, polyisobutylene, a butadiene/styrene copolymer or a butadiene/acrylonitrile copolymer. 15
4. A resilient composition according to claim 1, 2 or 3, wherein the active-hydrogen group-containing hydrocarbon polymer is a hydroxy-tipped hydrocarbon polymer.
5. A resilient composition according to any preceding claim, wherein the active-hydrogen group-containing hydrocarbon polymer has a molecular weight in the range 400 to 10,000. 20
6. A resilient composition according to any of claims 1 to 4, wherein the active-hydrogen group-containing hydrocarbon polymer has a molecular weight in the range 1000 to 3000.
7. A resilient composition according to any preceding claim, wherein the active-hydrogen group-containing hydrocarbon polymer has active hydrogen groups at least at or adjacent the ends of the molecules. 25
8. A resilient composition according to any preceding claim, wherein the elastomeric material comprises whole-tyre scrap.
9. A resilient composition according to any preceding claim, wherein the elastomeric material comprises natural rubber, styrene/butadiene rubber or a blend thereof. 30
10. A resilient composition according to any preceding claim, wherein the elastomeric material is in the vulcanised state.
11. A resilient composition according to any preceding claim, wherein the elastomeric material is non-cellular.
12. A resilient composition according to any preceding claim, wherein the particle size of the elastomeric material is in the range from particles having a maximum dimension of 3 cm to those which will not pass a 200 μ sieve. 35
13. A resilient composition according to any of claims 1 to 11, wherein the particle size of the elastomeric material is in the range from a maximum dimension of 1.5 cm to a maximum dimension of 1 mm. 40
14. A resilient composition according to any preceding claim, wherein the relative proportion by weight of elastomeric material and polymer matrix is in the range from 1:1 to 9:1.
15. A resilient composition according to any preceding claim, wherein the relative proportion by weight of elastomeric material and polymer matrix is about 5:1.
16. A resilient composition according to any preceding claim, wherein the polyisocyanate comprises methylene-bis-aniline diisocyanate. 45
17. A resilient composition according to any of claims 1 to 15, wherein the ratio of the number of functional NCO groups in the polyisocyanate to the number of active hydrogen groups in the active-hydrogen group-containing hydrocarbon polymer is in the range from 10:1 to 1:1.
18. A resilient composition according to any preceding claim, wherein the ratio of the number of functional NCO groups in the polyisocyanate to the number of active hydrogen groups in the active-hydrogen group-containing hydrocarbon polymer is in the range from 4:1 to 3:1. 50
19. A resilient composition according to any preceding claim, wherein the polymer matrix comprises a polyurethane, a polyurea or a polyamide.
20. A resilient composition according to any preceding claim, wherein the polymer matrix is the reaction product of an active-hydrogen group-containing hydrocarbon polymer, an organic polyisocyanate, moisture and a catalyst. 55
21. A resilient composition according to claim 20, wherein the catalyst is a tin compound.
22. A resilient composition according to claim 21, wherein the catalyst comprises stannous octoate or dibutyl tin dilaurate.
23. A resilient composition according to any preceding claim, wherein the polymer matrix includes carbon black. 60

24. A resilient composition according to claim 1 substantially as described in any one of Examples II to VI.
25. A resilient composition according to any preceding claim which is water permeable.
26. A resilient composition according to any preceding claim when used as a surfacing material.
- 5 27. A resilient composition according to any preceding claim when used as a sports surface. 5
28. A method of producing a resilient composition comprises dispersing a particulate elastomeric material in a polymer matrix which is a reaction mixture comprising an active-hydrogen group-containing hydrocarbon polymer and an organic polyisocyanate, and curing the matrix in the presence of moisture.
- 10 29. A method according to claim 28, wherein the elastomeric material is combined with the polymer-forming composition which is in the form of a prepolymer. 10
30. A method according to claim 28 or 29, wherein the active-hydrogen group-containing hydrocarbon polymer and organic polyisocyanate are liquid when combined.
31. A method according to claim 28, 29 or 30, wherein the elastomeric material is prevulcanised.
- 15 32. A method according to any of claims 28 to 31 having the feature defined in any one of claims 1 to 23. 15
33. A method according to claim 28 substantially as described in any one of Examples II to VI.

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